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# SULFATES IN THE ATMOSPHERE: A PROGRESS REPORT ON PROJECT MISTT*

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**Abstract**—The size and sulfate content of atmospheric aerosols and the rate and mechanisms for sulfate formation from sulfur dioxide in power plant plumes are reviewed. Emphasis is given to results from the recent USEPA study, Project MISTT (Midwest Interstate Sulfur Transformation and Transport). The rate of conversion of sulfur dioxide to sulfate aerosol in power plant plumes is low near the point of emission, but increases to several per cent $h^{-1}$ as ambient air mixes with the plume. Tall stacks reduce ground level concentrations of sulfur dioxide, resulting in a reduction of the amount removed by dry deposition. In urban plumes, which are well-mixed to the ground near the source, sulfur dioxide is removed more rapidly by dry deposition. Thus, tall stacks increase the atmospheric residence time of sulfur dioxide, which leads to an increase in atmospheric sulfate formation. These sulfate aerosols may be transported over distances of several hundred kilometers and produce air pollution episodes far from the pollution source.

## INTRODUCTION

Sulfate is a pollutant of note, having been linked in epidemiological and laboratory studies with adverse effects on human health (Amdur *et al.*, 1972; EPA, 1974). Epidemiological studies have, in fact, indicated that sulfate may be more toxic than sulfur dioxide or total suspended particulates. Sulfates are also known to be major contributors to reductions in visual range caused by atmospheric aerosols (Waggoner *et al.*, 1975). Studies of acid precipitation in Scandinavia (Bolin, 1971) have implicated sulfuric acid in a variety of adverse ecological effects.

The known adverse health effects of sulfur dioxide ($SO_2$) led to the control of this pollutant (PHS, 1969). Reduction in urban $SO_2$ emissions and concentrations effected by the mandatory use of low-sulfur fuels, however, were not accompanied by a proportional decrease in urban sulfate (EPA, 1975).

The observed lack of a proportional decrease has four possible explanations: (1) sulfates can be biogenic in origin, resulting from transformations of hydrogen sulfide, methyl disulfide and methyl mercaptans, which are natural products; (2) measured sulfate values are not real but anomalous, resulting from conversion of $SO_2$ to sulfates on filters used in sampling; (3) observed sulfates are primary pollutants produced from the combustion of high-vanadium oil or from combustion in small, inefficient furnaces; and (4) observed sulfates may be explained by the transformation–transport theory. Reductions in urban $SO_2$ emissions have been accompanied by increases in rural $SO_2$ emissions from new power plants located outside cities. $SO_2$ from these power plants may be transformed to sulfate in the atmosphere and transported over long distances to urban areas.

The fourth possibility, the transformation–transport theory, is supported by Scandinavian (Bolin, 1971) and U.S. studies (Wilson, submitted) and could account for the increased sulfate levels observed in rural areas and the static sulfate levels observed in urban areas in the U.S. (EPA, 1975). Early information on the rate of conversion of $SO_2$ to sulfate in power plant plumes suggested that the rate of conversion was too low to result in significant formation, and subsequent transport, of sulfate (Wilson, submitted). However, studies of the flux of sulfur out of various areas, e.g. studies by Smith and Jeffrey (1975) and of Waggoner *et al.* (1976), successfully showed that some of the sulfur transported from source areas like the United Kingdom arrived in Scandinavia as sulfates.

Interest by the Environmental Protection Agency in the transformation–transport theory, and the relevance of this theory to energy usage, led to a major expansion of existing studies with the establishment of Project MISTT. Project MISTT is funded with Federal Interagency Energy/Environmental Research and Development funds. The technical approach of Project MISTT is to study the transformations of $SO_2$ to sulfate in polluted air masses undergoing transport. The intent is to measure pertinent chemical and meteorological parameters with sufficient accuracy that they may be used with physical and mathematical models to derive rate parameters which characterize the transformation processes. This research should also give insight into transformation mechanisms and serve to guide laboratory studies of rates and mechanisms. The initial plans called for the

* Midwest Interstate Sulfur Transformation and Transport.



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study of power plant and urban plumes. However, during the program another type of pollutant transport was recognized and the program was expanded to include the 'blob'. This term refers to large-scale polluted air masses, apparently associated with anticyclones, in which pollution can build up during stagnant periods and be carried for long distances as the weather system moves.

This paper will discuss the technical and management approach to Project MISTT, describe the type of information obtained, review the important experimental findings, and discuss their implications for air pollution control policies.

## TRANSFORMATION MECHANISMS

Though they are not well understood, the mechanisms by which $SO_2$ is oxidized to sulfates are important because they determine the rate of formation of sulfate, the influence of the concentration of $SO_2$ on the reaction rate and, to some extent, the final form of sulfate. Atmospheric $SO_2$ may be oxidized to sulfur trioxide ($SO_3$) and converted to sulfuric acid aerosol, or it may form sulfite ions that are then oxidized to sulfate. Subsequent to the oxidation, sulfuric acid or sulfate may interact with other materials to form other sulfate compounds. The most important sulfate formation mechanisms identified to date are summarized in Table 1.

A key concern for air pollution control strategy is to determine whether $SO_2$ conversion is first order or zero order in $SO_2$. If the conversion is first order, then an 80% decrease in $SO_2$ emissions could lead to an 80% decrease in sulfate. If, on the other hand, we assume the conversion is zero order in $SO_2$ and that at the present time 10% of emitted $SO_2$ is converted to sulfate, then it could require a 98% reduction in $SO_2$ emissions to produce an 80% reduction in sulfate. In the latter case it becomes very important to determine if there are other pollutants that influence $SO_2$ conversion and that could be more easily controlled. For example, if heavy metal catalysis is important (Mechanism 5), better fly ash controls to limit primary aerosol emissions could be used to reduce sulfate.

Mechanisms 1 and 2 are first order in $SO_2$ and in sunlight. Mechanism 2 also depends on the composition of the background air because this will influence reactive species such as OH, $HO_2$, and $CH_3O_2$. Mechanisms 3, 4, 5 and 6 may be near zero order in $SO_2$, but depend strongly on the concentration of ammonia, oxidants, soluble catalytic metal ions, or particulate surface area. Mechanisms 3, 4, and 5 will be important only when liquid droplets can exist, i.e. under conditions of high water vapor content and high relative humidity.

It has been the intention of Project MISTT to study conditions conducive to the various types of mechanisms. However, experimental problems and weather conditions during field studies were such that we have more results applicable to the homogeneous mechanisms (1 and 2) than to the heterogeneous mechanisms (3–6).

## SIZE DISTRIBUTION

Studies (Whitby, 1975; 1978) over the past 5 years of the size distribution of particles in both sulfate aerosols and general atmospheric aerosols have led to important changes in our understanding of the behavior of aerosols such as sulfates in the ambient atmosphere. A schematic diagram of a typical atmospheric aerosol size distribution is shown in Fig. 1. The three principal modes (particle-size ranges), the

Table 1. Mechanisms by which sulfur dioxide is converted to sulfates (10)

| Mechanism | Overall reaction | Factors on which sulfate formation primarily depends |
|---|---|---|
| 1. Direct photooxidation. | $SO_2 \xrightarrow[\text{water}]{\text{light, oxygen}} H_2SO_4$ | Sulfur dioxide concentration, sunlight intensity |
| 2. Indirect photooxidation. | $SO_2 \xrightarrow[\text{organic oxidants, hydroxyl radical (OH) } HO_2, RO_2 \text{ radicals}]{\text{smog, water, } NO_x} H_2SO_4$ | Sulfur dioxide concentration, organic oxidant concentration, OH, $NO_x$, $HO_2$, $RO_2$. |
| 3. Air oxidation in liquid droplets. | $SO_2 \xrightarrow{\text{liquid water}} H_2SO_3$ | Ammonia concentration. |
| | $NH_3 + H_2SO_3 \xrightarrow{\text{oxygen}} NH_4^+ + SO_4^{2-}$ | |
| 4. Catalyzed oxidation in liquid droplets. | $SO_2 \xrightarrow[\text{heavy metal ions}]{\text{oxygen, liquid water}} SO_4^{2-}$ | Concentration of heavy metal (Fe, V, Mn) ions. |
| 5. Catalyzed oxidation on dry surfaces. | $SO_2 \xrightarrow[\text{carbon particle}]{\text{oxygen, water}} H_2SO_4$ | Carbon-particle concentration (surface area). |

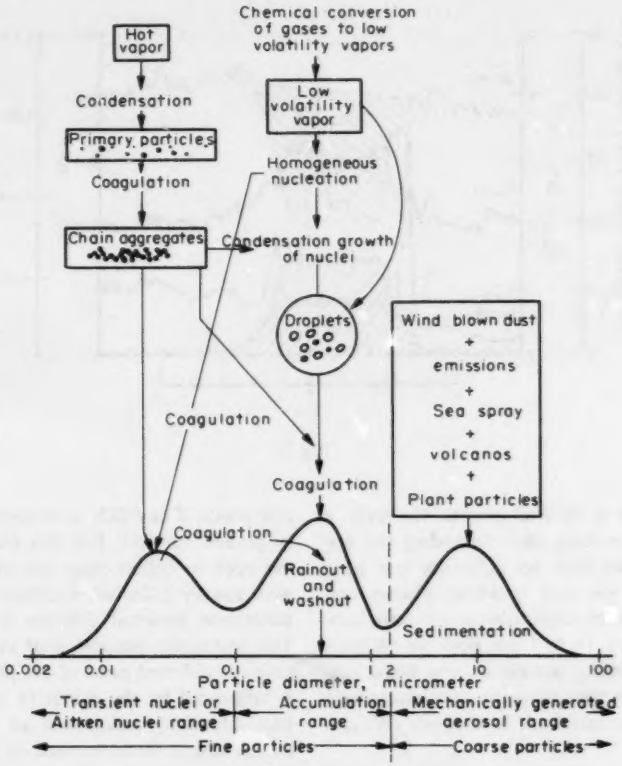


Fig. 1.

main sources of mass for each mode and the principal processes involved in inserting and removing mass from each mode are shown. Particles in the Aitken nuclei mode, 0.005–0.05 $\mu$m dia, are formed by condensation of vapors produced either by high temperatures or chemical processes. The accumulation mode, which includes particles from 0.05 to 2 $\mu$m dia, is formed by coagulation of particles in the nuclei mode and by growth of particles in the nuclei mode through condensation of vapors onto the particles. Coarse particles are formed by mechanical processes such as grinding or rubbing—e.g. soil, street dust and rubber tire wear—and by evaporation of liquid droplets. Accumulation mode particles do not continue to grow into coarse particles, however, because the more abundant small particles have a higher gas-aerosol collision rate and dominate the condensational growth process. Sulfates formed by the conversion of $SO_2$ are found in the accumulation mode; $MgSO_4$ from sea salt, $Na_2SO_4$ from paper pulping and $CaSO_4$ from gypsum are found in the 'coarse particle mode'.

## REVIEW OF PLUME STUDIES

Information on the rate of conversion of $SO_2$ to sulfate in power plant plumes was needed to quantify the contributions of power plants to atmospheric sulfates. A critical review of plume studies (Wilson, submitted) revealed no reliable information on conversion rates, and only two studies that provided information on the amount of $SO_2$ converted to sulfate. The early work of Gartrell *et al.* (1963) indicated little conversion of $SO_2$ to sulfate except at relative humidities greater than 75%. However, at high r.h., conversion of $SO_2$ to sulfate may occur either on the filter surface or within the aerosol particles collected on the filter. Therefore, Gartrell's results cannot be accepted unless verified by other techniques.

Investigators at the Brookhaven National Laboratory used two techniques to study sulfate formation in power plant plumes (Newman *et al.*, 1975a, b): the sulfur isotope technique and direct measurements of $SO_2$ and sulfate. The isotope technique is considered erroneous because of the presence of several competing reactions having different isotope effects (Wilson, submitted). The direct measurement of $SO_2$ and sulfate is considered to yield valid concentration ratios but this may not be adequate for the determination of conversion rates. The Brookhaven workers measured conversion from 0 to 8.5% $h^{-1}$ in coal-fired power plant plumes (Newman *et al.*, 1975a) and 0–26% $h^{-1}$ in oil-fired power plant plumes (Newman *et al.*, 1975b). The Brookhaven work has previously been interpreted to indicate an average conversion rate in coal-fired plumes of 1% $h^{-1}$ or less and a sub-

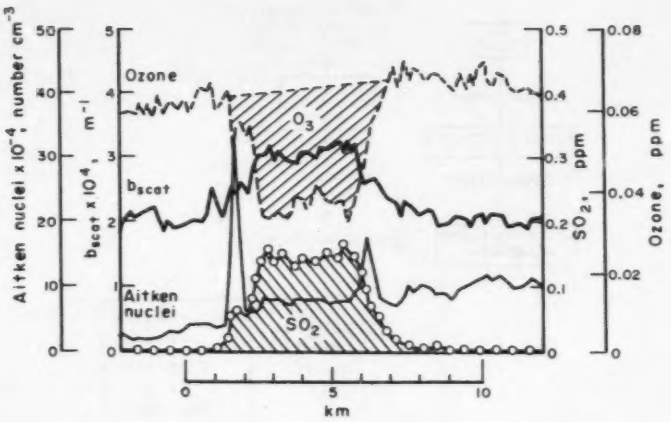


Fig. 2.

stantially higher rate in oil-fired plumes. However, a careful analysis of the data, after discarding the isotope results, indicates that no difference has been established between oil- and coal-fired plumes and that, depending on conditions, conversion rates substantially greater than $1\%\ h^{-1}$ are possible (Wilson, submitted). The sampling techniques and flight patterns used were such that an accurate measurement of the conversion rate could not be obtained (Wilson, submitted).

## EPA PLUME STUDIES

### *Program plan*

In order to obtain a better understanding of the physical and chemical processes occurring in power plant plumes, a new series of field studies were undertaken. During July and August of 1976 and July, August and February of 1975, extensive studies involving three-dimensional mapping of large plumes were carried out in the St. Louis area as part of the Midwest Interstate Sulfur Transport and Transformation Study (MISTT). Preliminary studies were conducted during July and August of 1973 and 1974.

These plume studies differed from earlier ones in that: (1) more gas and aerosol parameters were measured; (2) horizontal and vertical profiles were measured; (3) data were interpreted in terms of mass flows instead of concentration ratios; (4) the background air mixing with the plume was characterized; (5) the chemical composition and size distribution of the aerosols in the plume were determined; (6) measurements were made in approximately the same air mass as it moved downwind, and (7) measurements were made at the same distance downwind as the plume shape and structure changed with changes in meteorological conditions.

In previous studies, the fractional conversion of $SO_2$ to sulfate was calculated from the ratio of $SO_2$ to sulfate collected as integrated filter samples while circling in random portions of the plume at various downwind distances. This technique can overestimate conversion if any $SO_2$ is removed by dry deposition to ground surfaces. For this reason and because of the need to collect large amounts of $SO_2$, samples were usually collected in cohesive plumes which had undergone minimal dilution with background air. This technique can also lead to errors if conversion varies in different parts of the plume or if conversion is influenced by the extent to which the plume has been diluted by background air. That this can indeed be the case is demonstrated in Fig. 2, in which the nuclei formation rate is seen to be much greater at the edges of the plume than in the center. Although such a dramatic difference was not often observed, current interpretation of sulfate formation mechanisms suggests that the conversion rate will be higher in those portions of the plume, such as the edges, in which dilution has led to conversion of plume NO to $NO_2$ by background $O_3$ (Wilson *et al.*, 1975). To overcome these problems the EPA plume mapping studies were designed to measure $SO_2$ and sulfate mass flow rates at increasing distances from the source in both cohesive and well-mixed plumes.

Another problem which occurs when studies are limited to cohesive plumes has to do with the effect of sunlight on the $SO_2$ conversion process. The key reactant for conversion of $SO_2$ to sulfate is thought to be the hydroxical radical, with $HO_2$ and $RO_2$ becoming important in polluted air (Mechanism 2). The concentration of these species will be proportional to the sunlight intensity. Cohesive plumes occur in the morning and evening when, due to low sunlight intensity, there is insufficient thermal energy to cause rapid mixing of the plume with background air. Thus the lack of sunlight means no direct or indirect photochemical conversion (Mechanism 1–2). The lack of dilution results in low input of ammonia into the plume, causing the aerosols to become acidic, if liquid, or coated with $SO_2$ if solid, until no further $SO_2$ can be absorbed. Therefore heterogeneous reactions (Mechanisms 3, 4 and 5) can occur only to a limited extent. Studies of conversion in cohesive

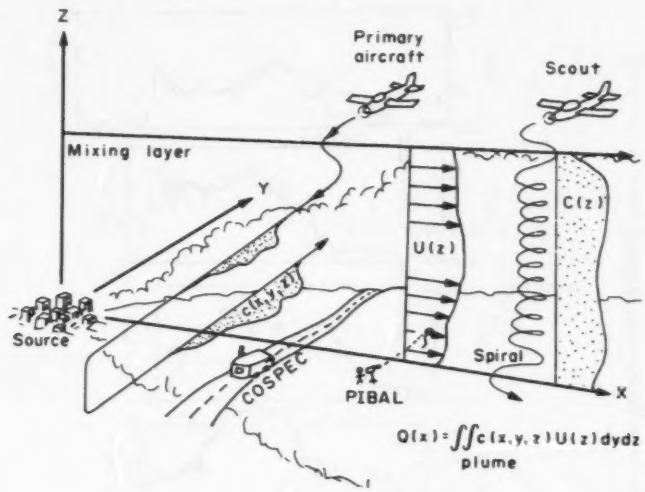


Fig. 3.

plumes therefore would be expected to show low reaction rates.

*Plume mapping program*

Two instrumented aircraft, an instrumented van, and three mobile single-theodolite pilot-balloon units were used in a coordinated measurement program (Fig. 3). The primary sampling platform was a single-engine aircraft equipped for continuous monitoring of the gaseous pollutants ($O_3$, NO, $NO_x$, $SO_2$) (Blumenthal *et al.*, 1978); three aerosol parameters (condensation-nuclei count, light-scattering coefficient and aerosol charge); several meteorological variables (temperature, r.h., dew point and turbulent dissipation); and navigational parameters. Particulate sulfur samples were gathered by a sequential filter-tape sampler equipped with a respirable-particle size separator. An array of four cascade impactors collected size-differentiated aerosol samples for later chemical and microscopic analyses. An optical counter and an electrical-mobility analyzer provided details of the *in situ* particle-size distribution of grab samples (White *et al.*, 1976a). During the summer 1976 study a twin engine aircraft was equipped for continuous monitoring of $O_3$, $SO_2$, light scattering coefficient, aerosol charge and navigational parameters, and for collection of aerosol samples with a sequential filter tape sampler.

An instrumented 'scout' aircraft located the plume, laid out the sampling path of the primary aircraft, and directed the three mobile pilot-balloon (pibal) units to their respective positions in the center and at the edges of the plume. Coordinated with the aircraft sampling, a van equipped with a correlation spectrometer (COSPEC) made lateral traverses under the plume and measured the integrated overhead burden of $SO_2$ and $NO_2$ (Vaughan, 1975). During summer 1975 a ground sampling station was located 100 km north of St. Louis. In cooperation with Project MISTT measurements were made by Argonne National Laboratory to characterize the structure and dynamics of the boundary layer in the area north of St. Louis. During summer 1976 a ground mobile sampling unit made measurements under the plume and COSPEC measurements were conducted from an airplane platform. The operations headquarters coordinated the mobile units by radio communication.

Data collected aboard the two aircraft and in the vans were recorded automatically at 1- to 10-s intervals on magnetic tapes for subsequent computer processing. The aircraft's instruments were calibrated before and after each flight. The aircraft data, which were originally recorded on magnetic tape cartridges, were transferred to nine-track tapes immediately after the flight. Calibrated constants were inserted, engineering units calculated, and strip charts generated within 24 h so that the data would be available for inspection and discussion prior to subsequent flights. This also ensured that any instrument malfunctions or errors in sampling design would be discovered immediately and could be corrected with minimal loss of needed data.

The flight pattern of the primary aircraft was designed to enable characterization of the plume at discrete distances downwind from the source. At each distance, horizontal traverses were made in the plume perpendicular to the plume axis at three or more elevations. These were supplemented by vertical spirals within and outside the plume. The continuous instruments monitored the distribution of pollutants along each pass. From the three-dimensional pollutant concentration field obtained in this manner, together with the vertical profiles of wind velocity measured every half-hour by the three pibal units, the horizontal flow rates of pollutants at each downwind distance were directly calculated. Since no continuous monitor for sulfate was available, the continuous light-scattering ($b_{scat}$) measurement was used as an indication of the

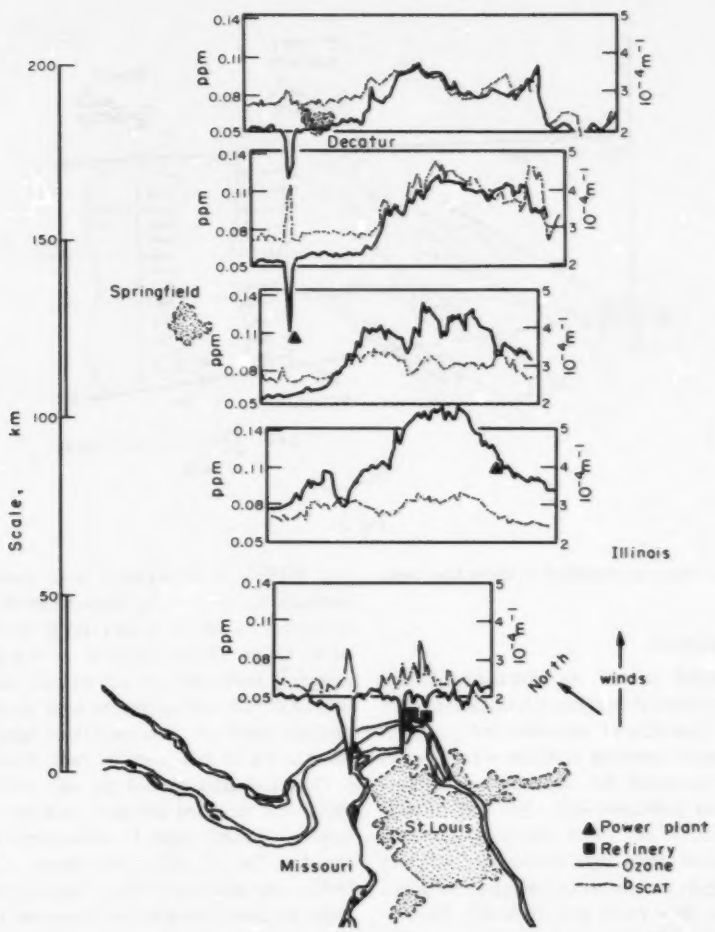


Fig. 4.

sulfate concentration distribution. Sulfate, collected in filter samples during each pass through the plume, was analyzed by the flash vaporization–flame photometric detection method—a new, highly sensitive technique modified for aircraft use (Husar *et al.*, 1975, 1977). The sulfate flow was calculated from the $b_{scat}$/sulfate concentration ratio, integrated over a pass, and the $b_{scat}$ flow. Similarly, $b_{scat}$-to-aerosol volume ratios were used to calculate an aerosol volume flow. From the change in flow rate with distance, it is possible to calculate transformation and removal rates for individual pollutants (Husar *et al.*, 1974, 1976). Under well-defined wind conditions (unidirectional, steady wind field), the reproducibility of the pollutant flow measurement was $\pm 20\%$.

*Urban plumes*

The techniques just described were used to map the three-dimensional flow of aerosols and trace gases in power plant plumes and in the air leaving the St. Louis area. It was found that under certain summer, daytime meteorological conditions the aggregate pollutant emissions from metropolitan St. Louis often formed a cohesive, well-defined 'urban plume' downwind of the city (Husar *et al.*, 1974, 1976; White *et al.*, 1976b). Such a plume can be identified in Fig. 4, which shows ozone concentrations and light-scattering coefficients measured within the mixing layer northeast of St. Louis on 18 July 1975 (White *et al.*, 1976b). The application of the plume mapping technique to this plume will be described as an example of the type of data and results obtained from Project MISTT.

On that day, the St. Louis plume incorporated the emissions of major coal-fired power plants at Labadie (Mo.) and Portage des Sioux (Mo.) and of a refinery complex near Wood River (Ill.), in addition to emissions from industries and automotive traffic of the St. Louis–East St. Louis urban area itself. The concentrated individual plumes immediately downwind of large combustion sources can be identified in Fig. 4 by their ozone 'deficits'; the depressed concentrations of $O_3$ in these plumes reflect the high concentration of NO in effluents.

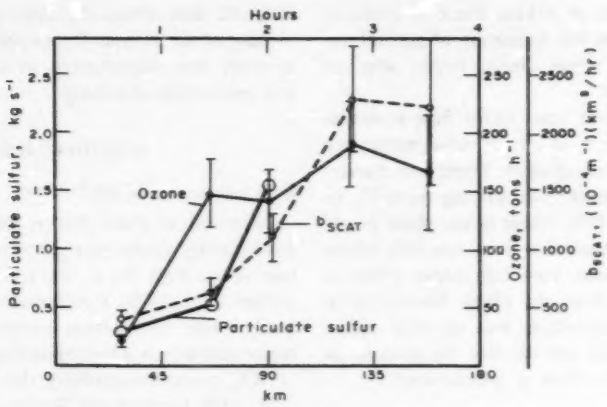


Fig. 5.

The width of the plume, approx 40 km, did not change much along its 150-km length. Apparently, horizontal diffusion at the boundaries of the urban plume is slower than might be predicted by Gaussian plume models. The amount of plume spreading is probably controlled by the amount of wind shear within the well-mixed layer. It appears likely that the elevated ozone concentrations in this plume and the reduced visibility caused by the plume were exported well beyond Decatur, Ill.

Unlike the primary pollutants NO and $SO_2$, ozone and light-scattering aerosols attained their maximum concentrations well downwind of St. Louis on 18 July 1975. The ozone and most of the aerosol were not emitted but were products of chemical and physical transformations in the atmosphere; their secondary origin is evident in Fig. 5, which shows flow rates of ozone and aerosol in the St. Louis plume increasing with distance from the city. The flow rates in Fig. 5 represent only the contribution of the St. Louis plume, and are calculated from the measured winds within the plume and from the difference between pollutant concentrations inside and outside the plume.

Based on a number of experiments in 1974 and 1975, the following features of the urban plume were observed to be typical: (1) The St. Louis plume significantly degraded the air quality of communities as far as 150 km from the city. (2) The most conspicuous components of the St. Louis plume 50 km or more downwind of the city were the reaction products formed along the way. (3) Most of the aerosol responsible for the high $b_{scat}$ and resulting decrease in visibility within the St. Louis urban plume was formed in the atmosphere.

The sulfate concentrations in the 18 July 1975 urban plume attained a maximum of 20 $\mu g\,m^{-3}$. This is not an extremely high value. On 29–30 July 1975 the urban plume was followed for 18 h and measurements were made both in the evening and the following morning. During this experiment sulfate concentrations of 60 $\mu g\,m^{-3}$ were measured, as shown in Fig. 6. This set of measurements demonstrates that at least under some conditions sulfate formation can exceed removal and dilution and can lead to the accumulation of very high sulfate concentrations.

*Sulfate budget*

By examining the total flow of sulfur—both $SO_2$ and sulfate—we can draw some interesting conclusions regarding the transformation and removal of $SO_2$ in the two classes of plumes, that is, power plant plumes and urban plumes (Husar *et al.*, 1976). Data were examined for those days in which the wind direction was such that the plumes of the rural power plants (tall stacks, >200 m) were well separated from the urban plume which contained emissions from low stacks (≤ 100 m) and near ground level sources. In such plumes, the total sulfur flow rate (gaseous plus particulate) has been found to decrease with distance. The pollutant flow rate, as determined from both the aircraft-measured concentrations and correlation spectrometer data, shows a decay in excess of the estimated experimental uncertainty of the methods (±20%).

Initial sulfur depletion in the urban plumes measured appeared to be equivalent to an exponential rate of decay with a characteristic (1/e) decay time of 3–4 h. Formation of new sulfate aerosol is undetec-

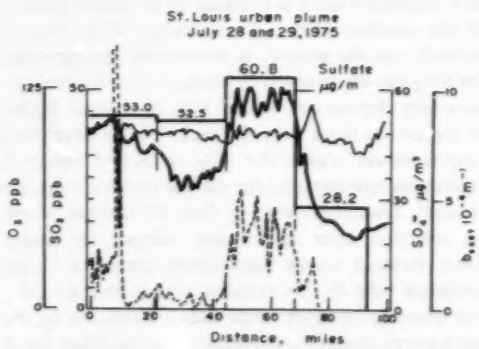


Fig. 6.

table up to a distance of 50 km. There is evidence that during the daytime the formation of aerosol, including sulfate in an urban plume, begins after an ageing time of 1 or 2 h.

In power plant plumes total sulfur flow measurements frequently showed no loss of sulfur within the limits of experimental uncertainty. There was conversion of $SO_2$ to sulfates at rates varying from $\frac{1}{2}\%$ to $5\%\ h^{-1}$ (Husar *et al.*, 1978). These power plant plume measurements demonstrate that there was little removal of the sulfur emitted from tall stacks within a region of 50–100 km from the plant. During these measurements, dry deposition was minimal either because the plumes had not touched the ground or because they were very dilute at ground level.

*Removal processes*

It is important to understand that most sulfate aerosol is secondary, i.e. formed by gas-to-particle conversion in the atmosphere after emission, and occurs in the accumulation mode. Particles in this size range have very long lifetimes. Some confusion has existed regarding the relative removal rates for $SO_2$ and sulfate aerosol by deposition. The deposition velocity of aerosols depends on the particle size and reaches a minimum in the accumulation size range of 0.1–1.0 $\mu$m. The deposition velocity of gaseous $SO_2$ depends on the chemical reactivity of the surface. Both deposition velocities depend on the friction velocity and the surface roughness. However, since the diffusion of accumulation mode aerosols through the surface boundary layer (0.001–1 cm) is much slower than the diffusion and surface reaction of an $SO_2$ molecule, the deposition velocity of sulfate aerosol is usually smaller than for gaseous $SO_2$ (Sehmel, 1971, 1973; Sehmel and Hodgson, 1974). Consequently, though $SO_2$ is removed fairly rapidly by dry deposition on soil, vegetation and other surfaces, the removal processes become slower once the $SO_2$ has been converted to sulfate. Therefore, sulfates can travel long distances before their removal by fallout, rainout, or deposition.

*Effects of tall stacks*

These aspects of reaction mechanisms, aerosol size and deposition rates are critical to an understanding of the possible effects of tall stacks. When $SO_2$ is emitted near the ground, as from home heating units, the $SO_2$ can be removed by surface removal mechanisms (dry deposition). When $SO_2$ is emitted higher in the air, as from the tall stacks of fossil-fuel-fired electric power plants, the $SO_2$ is diluted before it reaches the ground, and the surface removal rates are reduced. Emissions may, in fact, be trapped above an inversion layer and remain trapped for hours. Thus, elevated stacks theoretically permit a longer residence time in the ambient atmosphere for $SO_2$ and promote fine particulate sulfate formation by the mechanisms discussed previously. On the other hand, they provide for increased dilution of the sulfate and $SO_2$ and thus reduce the impact of emissions in the vicinity of the source. Continued studies are planned to study this phenomenon as a function of time of day and extent of mixing.

## SCIENTIFIC RESULTS

*Reaction rates and mechanisms*

In the power plant plumes which have been completely analyzed the rate of conversion of $SO_2$ to sulfate varied from $\frac{1}{2}\%$ to $5\%\ h^{-1}$ (Husar *et al.*, 1978; Gillani *et al.*, 1978). Condensation nuclei counts and aerosol size distribution profiles indicate that the major pathway is a homogeneous reaction, first order in $SO_2$, probably involving the OH radical (Whitby *et al.*, 1978; Cantrell and Whitby, 1978). The pollutant profiles, in power plant and urban plumes, resemble those observed in chamber studies and suggest that the current chemical kinetic models can be used to calculate sulfate formation (Miller *et al.*, 1978). The reaction rate certainly depends on sunlight intensity and appears to also depend on water vapor concentration, background ozone levels and the extent to which the plume has mixed with background air (Husar *et al.*, 1978).

Heterogeneous reactions may be important at night, in clouds, or other conditions during which high water vapor content and high r.h. may lead to the existence of liquid droplets. Attempts to make night-time measurements during summer 1975 were frustrated by difficulties in locating the plume. The use of lidar during summer 1976 allowed us to locate the plume but unusually dry conditions led to night-time relative humidities substantially lower than normal. Therefore, the data analyzed to date do not allow any conclusions regarding heterogeneous reactions.

*Plume study techniques*

One of the most important advances has been the realization that a plume measurement must be treated as a multi-dimensional problem. In addition to its extent in the horizontal and vertical direction and the downwind distance we must consider time as a fourth dimension. We must be concerned not only with the time at which the plume is measured but also the time at which the plume was emitted and the history of the plume since it was emitted. For example, it may have been a cohesive plume prior to measurement or it may have been highly diluted with background air; it may have been isolated above the mixing layer or it may have been well mixed to the ground; it may have traveled at night, under cloud cover, or in bright sunlight. Much of the early work on plumes has yielded misleading values because the measurements were made only in cohesive plumes early in the morning or late in the evening.

The use of mass flow measurement, in addition to $SO_2$/sulfate ratio measurements, permits a determina-

tion of the loss of $SO_2$ by ground deposition. This technique makes it possible to determine rates during periods when the plume is well mixed to the ground and the $SO_2$/sulfate ratio measurements would give erroneously high rates. The development of a sulfate analytical technique with sufficient sensitivity for a measurement integrated over one pass through a plume made possible the determination of sulfate mass flows. The measurement of size distribution profiles permitted measurements of aerosol volume flows for comparison with sulfate mass flows and gave insight into the type of reaction mechanism.

*Transport distances*

The time and distance over which an air mass maintains its integrity depends on its initial size and the meteorological conditions. Power plant and urban plumes have been tracked for 300 km (Gillani *et al.*, 1978). These plumes maintain their integrity and high pollutant concentrations for much longer times and farther distances than was originally expected. During stable night-time conditions, the cohesive plume is frequently caught in a nocturnal jet which carries it along at as much as twice the normal wind speed (Smith *et al.*, 1978). Gaussian plume models are satisfactory for the first few tens of km but beyond that wind shear seems to play the dominant role in determining dilution. In urban plumes wind shear is clearly the determining factor. Using visibility isopleths and long range trajectories it has been possible to track 'blobs' (hazy air masses associated with stagnating anticyclones) for over a 1000 km (Lyons *et al.*, 1978; Husar *et al.*, 1976).

*Models*

Models, of several levels of complexity, have been developed for the calculation of secondary pollutant concentrations in power plant and urban plumes. These include a reacting plume model with relatively simple mixing parameters but with provisions for aerosol formation, coagulation and growth and a multi-step chemical kinetic model (Brock *et al.*, 1978). In addition, a model has been developed using a sulfate formation rate which is a function of sunlight intensity and which has more sophisticated meteorological terms including multi-layers for vertical diffusion and dry deposition (Gillani, 1978).

*Future work*

The present study has concentrated mainly on sulfate, ozone and light scattering. It is planned to extend the EPA plume studies to include measurements of organic aerosols and vapors and nitrate aerosols and vapors, such as nitric acid. In order to determine the importance of heterogeneous reactions, more work is needed under conditions of high r.h. and high water vapor content which are conducive to heterogeneous reactions. In general, more information is needed to provide better statistics on the parameters which influence reaction rates in power plant and urban plumes.

The 'blob' is a special challenge. New techniques are required to develop models and to study transformation and transport in such systems.

## SUMMARY

Earlier work had shown that the rate of conversion of $SO_2$ to sulfate in power plant plumes was slow except at very high r.h. In the recent EPA program, consistent conversion of from $\frac{1}{2}$ to 5% $h^{-1}$ at normal levels of r.h. has been measured. The conversion of $SO_2$ to sulfate aerosol in power plant plumes is slow in the early part of the plume; that is, close to the point of emission. As ambient air mixes with the plume, the rate of conversion increases. Thus tall stacks reduce ground-level concentrations of $SO_2$ but increase sulfate aerosol formation by reducing surface losses of $SO_2$ and by increasing the atmospheric residence time, which results in increased $SO_2$-to-sulfate conversion. In urban plumes, which are well-mixed to the ground, $SO_2$ may be removed by reaction with plants and by deposition. The $SO_2$ dry deposition rates vary with vegetation, with the nature of the surface and with time of year.

Power plant and urban plumes have been sampled out to 300 km from their sources. Sampling at these distances revealed that sulfate, generated from $SO_2$ in power plant plumes, and ozone, generated from hydrocarbons and nitrogen oxides in urban plumes, may be transported at least hundreds of km and may cause air pollution episodes far from the source of pollution. Air pollution, due to secondary pollutants such as sulfates and ozone, cannot be controlled by the government entity where the air pollution impact actually occurs. Therefore, current concepts of air quality control regions must be revised to take into account the long-range transport of secondary pollutants.

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## APPENDIX

*Program management*

Project MISTT is an integrated scientific research program based on the formation of a team of the most competent scientists in the field. From the nucleus of a few aerosol scientists who first worked together in Los Angeles in 1969, a team comprising many disciplines and interests has slowly been developed. Over the years expertise in atmospheric chemistry, meteorology, and chemical and diffusion modelling has been added to the group. Although maximum freedom in program planning and execution is encouraged, strong central direction is maintained to ensure that the Environment Protection Agency's needs are satisfied.

The senior investigators are listed below.

William E. Wilson, Project Director; Environmental Protection Agency.

R. B. Husar, Field Director; Washington University.

Don Blumenthal, Aircraft Operations; Meteorology Research, Inc.

K. T. Whitby, Aerosol Dynamics; University of Minnesota.

Seventeen institutions have been involved in the program at various levels of participation. The institutions, the principal investigators, and a brief description of their responsibilities are given below:

Argonne National Laboratory: Paul Frenzen, boundary layer structure and dynamics; Bruce Hicks, dry deposition rates (ANL work was cosponsored by ERDA.)

Battelle Columbus Laboratories: David Miller, outdoor smog chamber measurements of sulfate formation rates in St. Louis; Peter Jones, Gas chromatographic–mass spectrometric measurements of organic vapors.

California Institute of Technology: Sheldon Friedlander; Development of a supersensitive sulfate measurement technique, sulfate measurements—1974.

Environmental Measurements, Inc.: William Vaughan; COSPEC measurements.

Environmental Quality Research: William Dannevik; Forecasting and other meteorological support, Dry deposition studies.

EPA-Las Vegas: Roy Evans; Helicopter measurements, winter 1976, aircraft lidar observations, summer 1976.

EPA-Research Triangle Park: W. E. Wilson and Jack Durham; Program management; Tom Ellestad; Instrument calibration, data transfer, measurements in EPA mobile lab.

Florida State University: John Winchester and William Nelson; Aerosol measurements using the FSU 'Streaker' sampler with PIXIE analysis.

IIT Research Institute: Ron Draftz; Optical and electron microscopy.

Meteorology Research, Inc.: Don Blumenthal, Jerry Anderson, Warren White and Ted Smith; Aircraft measurements, data analysis, meteorological interpretation.

University of Minnesota: K. T. Whitby and Bruce Cantrell; Aerosol size distribution measurements, aerosol dynamics, ground measurements, data analysis and interpretation.

Rockwell International Science Center: Al Jones; Pilot balloon operations.

Stanford Research Institute: Ed Uthe; Ground-mobile lidar operations.

University of Texas: Jim Brock; Effects of charge on aerosol deposition, reactive plume models.

Washington State University: R. Rasmussen and R. Chatfield; Detailed hydrocarbon analysis, interpretation of ozone and hydrocarbon data.

Washington University: R. B. Husar; Field Director, data analysis and interpretation; Noor Gillani; Data manager and model development; Janja Husar; Sulfate determinations.

University of Washington: R. Charlson and A. Waggoner; Ground-based measurements and data interpretations, sulfate species measurement, air mass trajectories.